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# Phenolic acetals from lignins of varying compositions via iron(III) triflate catalysed depolymerisation

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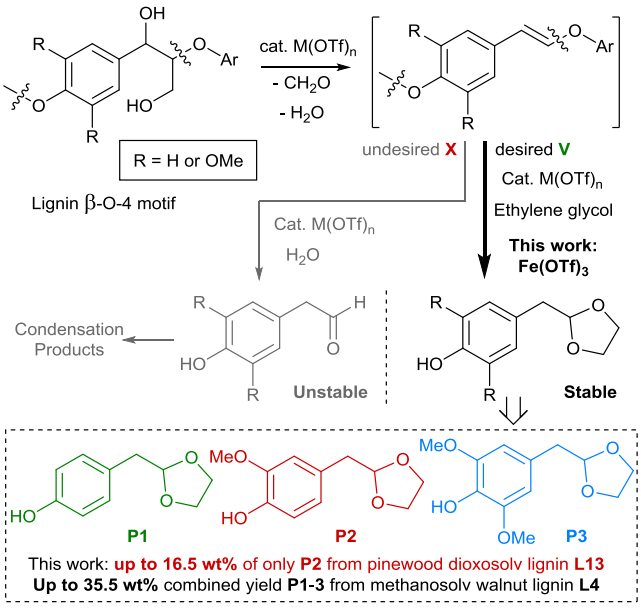
Peter J. Deuss,[a,b*] Christopher S. Lancefield,[c] Anand Narani,[a] Johannes G. de Vries,[a,d] Nicholas J. Westwood,[c] Katalin Barta[a*]

Lignin is a highly abundant, renewable aromatic polymer that can potentially be produced in large quantites from lignocellulosic biorefineries. Thus valorisation of this renewable resource by production of aromatic chemicals would be highly desirable and it is especially important to achieve high yields of these products. In this regard, not only the catalytic method used should be highly selective, but we must better understand possible correlations between the structure of the lignin used, and the yield of useful products. Here, we demonstrate that lignins obtained from a range of different biomass sources and pretreatment methods can be successfully depolymerized using iron(III) triflate in the presence of ethylene glycol to give p-(1,3-dioxolan-2-yl)methyl substituted phenols. 27 lignins, obtained from 13 different pretreatment methods, were examined in this study. Up to a combined 35.5 wt% yield of acetal products was obtained from a β-aryl ether rich organosolv lignin and the best yield of a single component (16.5 wt%) was achieved starting from pine lignin. Much lower yields were obtained from technical lignins which were low in β-aryl ether content, whilst a range of organosolv lignins of intermediate β-aryl ether content gave intermediate yields of acetal products. Overall, correlations were found between the product distributions and yields, and structural data of the parent lignins obtained from 2D HSQC NMR analysis.

## Introduction

The implementation of a profitable and sustainable lignocellulose-based biorefinery relies on the optimal valorisation of all biomass components.[1] Lignin, a major component (15-40%) of lignocellulosic biomass, has been identified as a key resource to access aromatic chemicals.[1d,1e,2] However, the efficient depolymerisation of this aromatic biopolymer to monomers has proved troublesome.[1d,2a,3] In the last few years, many research groups have shown elegant approaches to address this challenge,[1d,3,4] however very few methods have displayed satisfactory yields and general applicability. We and others have recently highlighted the importance of stabilizing reactive intermediates formed during the acid catalysed depolymerisation of lignin, for example using HOTf, metal triflates and other acids.[5]

In particular, the capture of the released aldehydes as acetals was successful in providing good yields of phenolic monomers from both model compounds and lignin.[5a,5b,5d,5g,5h] Such phenolic acetals have recently been shown to allow access to lignin based epoxy resins with high glass transition temperatures, highlighting their potential utility as renewable aromatic building blocks.[6]




Scheme 1 Acid catalysed depolymerisation of lignin with and without ethylene glycol trapping.

[a] Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands, E-mail: k.barta@rug.nl
[b] Department of Chemical Engineering (ENTEG), University of Groningen, Nijenborgh 4, 9747 AG, Groningen, the Netherlands, E-mail: p.j.deuss@rug.nl
[c] School of Chemistry and, Biomedical Science Research Complex , University of St Andrews and EaStCHEM, North Haugh, St Andrews, Fife, KY16 9ST, United Kingdom, E-mail: njw3@st-andrews.ac.uk
[d] Leibniz-Insitut für Katalyse e.V. , Universität Rostock, Albert-Einstein-Straße 29a, 18059 Rostock, Germany, E-mail: johannes.devries@catalysis.de

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Table 1. Overview of lignin extraction yields by weight using different lignin sources and extraction conditions.

| # | Lignin | Source | Extraction Procedure | Yields (wt%)[a] | Linkages (Per 100 C9 units)[b] | | | C9-types(%)[b] | | | Ref/source |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Total β-O-4[c] | β-β | β-5 | S | G | H | |
| 1 | **L1** | Walnut | MeOH Procedure 1 (total) | 11 | 13 | 4 | 5 | 63 | 32 | 4 | |
| 2 | **L2** | Walnut | DCM soluble (**L1**) | 3 | 25 | 6 | 8 | 65 | 29 | 6 | 5b |
| 3 | **L3** | Walnut | DCM insoluble (**L1**) | 8 | 48 | 3 | 11 | 45 | 38 | 17 | |
| 4 | **L4** | Walnut | MeOH Procedure 2 | 6 | 62 | 5 | 9 | 47 | 42 | 11 | This work |
| 5 | **L5** | Pinewood | MeOH Procedure 1 | 2 | 11 | 1 | 10 | 0 | 100 | 0 | 5b |
| 6 | **L6** | Pinewood | MeOH Procedure 1 | 2 | 12 | 4 | 10 | 0 | 100 | 0 | |
| 7 | **L7** | Walnut | EtOH | 6 | 58 | 5 | 10 | 47 | 41 | 12 | 7 |
| 8 | **L8** | Douglas Fir | | 6 | 52 | 2 | 13 | 0 | 100 | 0 | |
| 9 | **L9** | Walnut | BuOH | 32 | 41 | 3 | 3 | 73 | 25 | 2 | |
| 10 | **L10** | Beech | | 21 | 50 | 4 | 1 | 82 | 18 | 0 | 7 |
| 11 | **L11** | Douglas Fir | | 17 | 52 | 0 | 6 | 0 | 100 | 0 | |
| 12 | **L12** | Walnut | Diox. Procedure 1 | 1 | 23 | 6 | 22 | 31 | 38 | 31 | 5a |
| 13 | **L13** | Pine | Diox. Procedure 2 | 3 | 43 | 3 | 20 | 0 | 100 | 0 | This work |
| 14 | **L14** | Pine | | 3 | 33 | 3 | 18 | 0 | 100 | 0 | |
| 15 | **L15** | Oak | | 12 | 41 | 6 | 3 | 84 | 16 | 0 | 7 |
| 16 | **L16** | Barley | | 4 | 45 | 2 | 9 | 33 | 57 | 9 | This work |
| 17 | **L17** | Birch | | 10 | 45 | 6 | 2 | 88 | 12 | 0 | 4f |
| 18 | **L18** | Oak | CIMV | 6 | 43 | 5 | 4 | 74 | 26 | 0 | This work |
| 19 | **L19** | Beech | Technical EtOH | - | 11 | 3 | 3 | 68 | 32 | 0 | Commercial |
| 20 | **L20** | Poplar | | - | 4 | 2 | 3 | 59 | 41 | 0 | |
| 21 | **L21** | Spruce | | - | 2 | 1 | 5 | 0 | 100 | 0 | In kind |
| 22 | **L22** | Mix/Unk. | | - | 13 | 3 | 2 | 66 | 34 | 0 | |
| 23 | **L23** | Softwood | Industrial Kraft | - | 6 | 1 | 2 | 0 | 100 | 0 | Commercial |
| 24 | **L24** | Softwood | | - | 4 | 3 | 1 | 0 | 100 | 0 | In kind |
| 25 | **L25** | Mix/Unk. | | - | | | Insoluble | | | | |
| 26 | **L26** | Mix/Unk. | Industrial Soda | - | 3 | 1 | 1 | 48 | 40 | 12 | Commercial |
| 27 | **L27** | Mix/Unk. | Industrial Sulfonate | - | | | Insoluble | | | | |

[a] Relative to the total weight of the lignocellulose starting material

[b] As determined by 2D HSQC NMR, rounded to whole numbers

[c] Total of β-O-4-αOH and β-O-4-αOR

The major aromatic products obtained from the acidolysis of lignin by triflic acid or metal triflate salts in the presence of ethylene glycol are C2-1,3-dioxolane phenolics (**P1**-**P3**) originating from the *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) subunits of lignin, respectively (Scheme 1).[5a,5b,5d] In this contribution, we investigate the mild depolymerization of a wide variety of lignins via this method and focus specifically on establishing correlations between the structures of the lignins used and the yields of aromatic monomers obtained. We demonstrate, that especially high yields of **P1-P3** can be obtained with lignins rich in high β-aryl ether linkages. Aromatic dimers have also been identified and a preliminary structural investigation of the residual material left after the depolymerisation is presented.

## Results and discussion

### Isolation and characterization of lignins

In order to test our lignin depolymerisation methodology and study structure-reactivity relationships a small library of different lignins **L1**-**L27** were utilized. These contained "in-house lignins isolated from different lignocellulose sources using different organosolv extraction procedures **L1**-**L18** (Table 1) on laboratory scale. Organosolv extraction is a relevant

fractionation technique as it allows for separate valorisation of lignin, hemicellulose and cellulose, however the process parameters can have significant influence on the lignin quality.[1d] To obtain lignins of relatively high quality mostly mild processing conditions (relatively low acid/temperature) were selected. **L1**-**L4** are walnut shell methanosolv lignins of which **L2** and **L3** are the dichloromethane soluble and insoluble fractions of **L1** (170 °C, no acid).[5b] **L4** was extracted under acidic but lower temperature conditions (90 °C, 0.2 M HCl). The latter gave a lower yield of isolated lignin (6 vs 11 wt%), but one with a remarkably high β-aryl-ether content of 62 linkages per 100 $C_9$ units; the highest encountered in this study (*vide infra*). **L5** and **L6** are two different batches of pinewood methanosolv lignins (170 °C, no acid).[5b] **L7** and **L8** are ethanosolv lignins extracted from walnut shells and Douglas fir wood (reflux, 0.2 M HCl).[7] **L9**-**L11** are *n*-butanosolv lignins obtained from walnut shells, beech and Douglas fir wood (reflux, 0.2 M HCl, 32 wt% **L9**, 21 wt% **L10**, 17 wt% **L11**).[7] **L12**-**L17** are dioxasolv lignins from walnut shells[5a], pine wood (2x), oak wood[7], brewers' spent grains (barley) and birch wood[4f] (**L12**: reflux, no acid; **L13**-**L17**: reflux, 0.2 M HCl). **L18** was obtained by extraction of oak wood with a mixture of formic acid, acetic acid and water followed by a mild base hydrolysis (104 °C, formic acid/acetic acid/water 3 : 5 : 2 then 0.5 M NaOH, 6 wt%). As can be seen, the yield was highly dependent on the solvent, procedure and biomass source used ranging from 1 to 32 wt% based on the initial amount of lignocellulosic material used (Table 1). In particular, as we previously reported, lignins obtained by *n*-butanol extraction can be isolated in excellent yields.[8]

Additionally, several lignins were obtained from external sources. These are lignin that are already produced in current biorefinery setups of different scales and stages of development, but typically focus on optimal yield and purity of the carbohydrate fractions.[1d] **L19**-**L22** are technical lignins obtained by ethanosolv processes with different lignocellulosic biomass sources (**L19** beech, **L20** poplar, **L21** spruce wood from ECN, The Netherlands[9] and **L22** lignin from the Alcell process[10]). **L23**-**L27** are industrial lignins (**L23** Indulin-AT, **L24** Kraft), **L25** Alkali Kraft Aldrich, **L26** soda P1000 and **L27** lignosulfonic acid sodium salt Aldrich).

All these lignins were analysed by GPC to determine their molecular weight distribution and characterized using 2D-NMR to determine their structure in terms of H : G : S ratio and the quantities of major linkages (Tables 1 and S3, Fig. 1a and S24-42). Overall, the most remarkable difference between the "in-house" produced organosolv and the technical/industrial lignins was the overall β-aryl ether content ranging from 13 to 62 linkages per 100 $C_9$ units for the former and from 2 to 13 for the latter, as determined by 2D-HSQC NMR analysis (Table S3).[4f,11] One thing of note here is that, with the exception of the *n*-butanol extraction procedure, all organosolv processes used to produce our "in-house" lignins gave relatively low yields. Additionally, in all cases when alcoholic solvents were used in the extractions α-etherified β-O-4 linkages were observed, being particularly abundant under acidic conditions.

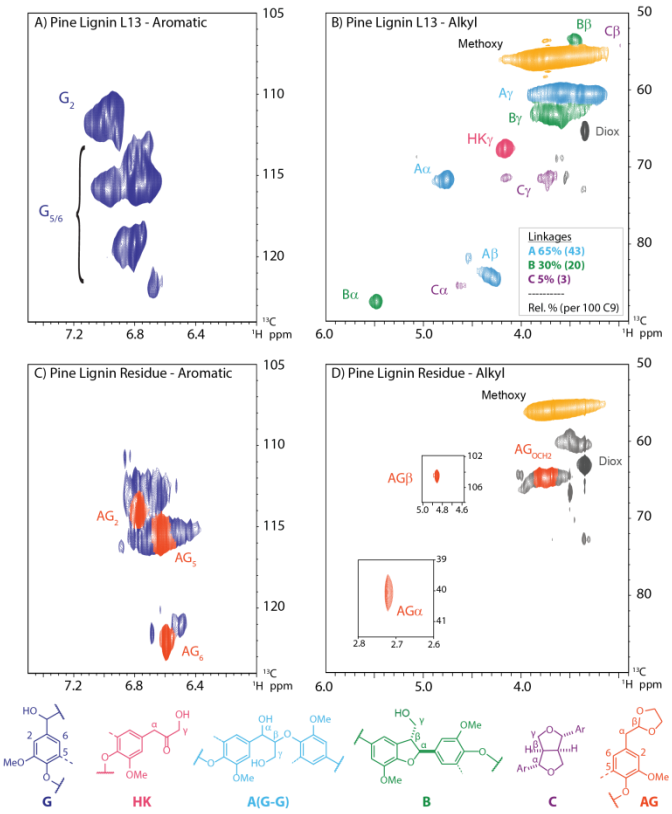



Fig. 1 A) aromatic region of the 2D-HSQC NMR spectrum of pinewood dioxasolv lignin **L13** and B) alkyl region. C) The aromatic region of 2D-HSQC NMR spectrum[12] of the 1,4-dioxane soluble/DCM insoluble residue obtained from the depolymerisation of **L13**, D) alkyl region showing 1,3-dioxolane end-groups.

**$Fe(OTf)_3$ catalysed depolymerisation of beech ethanosolv (L19) at varying reaction conditions**

Recently, we established a very efficient procedure for the production of a single set of phenolic C2-acetals from lignin using HOTf[5a,5b] and metal triflates[5d,5h] via cleaving the lignin β-O-4 linkages.[8] As we have previously shown that $Fe(OTf)_3$ gave the highest monomer yields[5d] and is easily handled compared to triflic acid we decided to use it in this study.[13] Initially, using technical beech ethanosolv lignin (**L19**), which was available to us in good quantities, we studied the effect of the catalyst concentration, reaction time and temperature on the yield of **P2** and **P3** (Fig. 2).

The results showed the minimum amount of catalyst required for an efficient depolymerisation reaction lies between 2,5 and 5 wt% (Fig. 2a). Above 5 wt% a small decrease in yield of **P2**-**3** was observed likely due to instability of the products formed. A similar apparent instability was also observed with increasing reaction time, with maximum yields obtained after 15 minutes (Fig 2b). By increasing the reaction temperature a small increase in **P2**-**3** yield was observed which dropped drastically at a temperature higher than 160 °C (Fig. 2c). In these experiments only **P2** and **P3** and no **P1** are observed as

products. This relates to the composition of lignin **L19,** which contains only G and S units. According to HSQC NMR analysis these are present in a 32 to 68 ratio respectively, a slightly higher than expected molar ratio of **P2** and **P3** (41 : 59 respectively) indicating relatively favourable formation of **P2** compared to **P3** from **L19**. The deviation between the G:S ratio and **P2**:**P3** ratio could be partly explained by a non-equal distribution of β-aryl ether linkages and the predominance of S-S β-β units (syringaresinol) compared to G-G or S-G variants in hardwood lignins.[14] In time and with the increase of reaction temperature the ratio **P2** to **P3** slowly increased (from 42:58 to 40:60 and from 43:57 to 39:61 respectively) indicating that **P3** although formed in lesser amount seems more stable than **P2**. Overall, this lignin gave relatively low monomer yields, which was later shown to be the result of the low amount of β-aryl ether linkages (*vide infra*). The residual material was analysed by GPC and was surprisingly shown to be of slightly higher molecular weight when compared to the starting lignin and showed very limited variation between the different reaction conditions (Figures S26 and S27). For the purpose of this study we settled on conditions of 10 wt% $Fe(OTf)_3$, at 140 °C for 15 minutes for all further reactions to balance out reactivity with product stability.

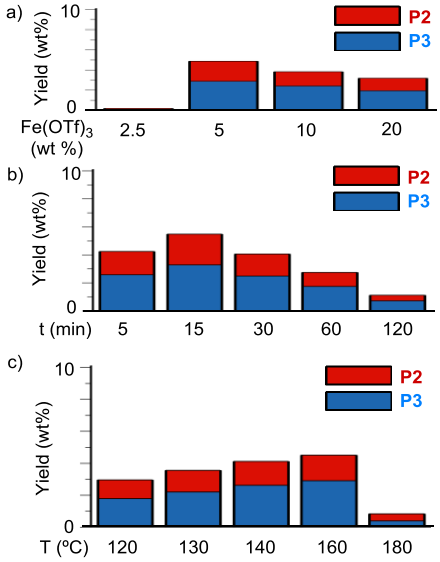
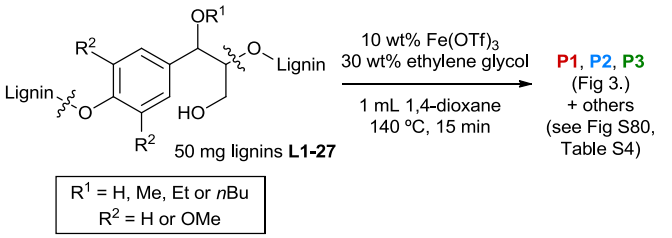



Fig. 2 $Fe(OTf)_3$ catalysed depolymerisation of 50 mg **L19** in 1,4-dioxane and 30 wt% ethylene glycol at a) varying catalyst concentrations using 140 °C, for 30 min., b) varying reaction time using 10 wt% $Fe(OTf)_3$, 140 °C and c) varying temperature using 10 wt% $Fe(OTf)_3$, for 30 min.

**$Fe(OTf)_3$ catalysed depolymerisation of lignins L1-27**

**General depolymerisation procedure.** 50 mg of the different lignins **L1**-**27** were depolymerized using catalytic $Fe(OTf)_3$ in 1,4-dioxane containing ethylene glycol (Scheme 2). After the reaction acetal products were extracted from the crude dried material allowing for the quantification of **P1**-**P3** by GC-FID and detection and quantification of other products by GC-MS (Table S4, Fig. S80). GPC-data revealed that indeed the low-molecular weight material is extracted and high molecular weight material is found in the residue (Fig. S45-S70). When the GPC graphs of the crude mixtures were compared to the graphs of the starting lignins in most cases overall lowering of the molecular weight is observed indicating depolymerisation. Nevertheless, in some cases higher molecular weight material is also formed indicating that not all condensation to higher molecular weight material is suppressed.




Scheme 2 $Fe(OTf)_3$ catalysed depolymerisation of different lignins in the presence of ethylene glycol.

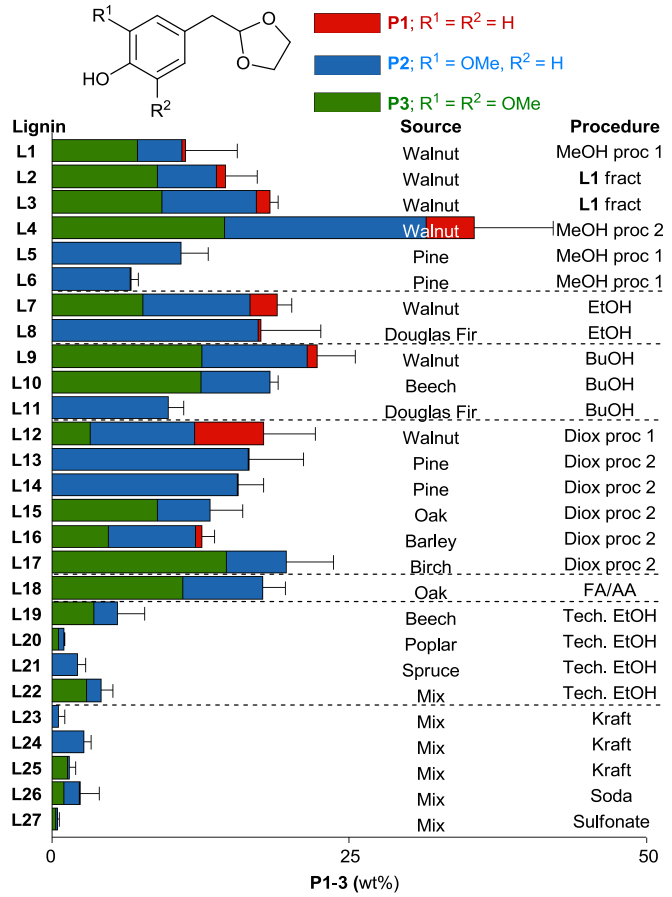



Fig. 3 Yields of **P1**-**P3** determined in the low-molecular weight fractions of product mixtures obtained after $Fe(OTf)_3$ catalysed depolymerisation of 50 mg of lignins **L1**-**L27** (Conditions in Scheme 2, averages for 2-4 experiments, error bars indicate the standard deviation of the total yield **P1**-**P3**).

**Yields of main monomeric products P1-3.** Fig. 3 shows the yields of **P1-3**, which were found as the main monomeric products obtained from the depolymerisation of **L1-27.** The relative quantities of **P1-3** were found to be generally in agreement with the original S/G/H ratios in the parent lignins (Fig. S72) with some small deviations. As shown in Fig. 4, the measured G/S ratio determined by NMR correlates nearly 1:1 to the molar ratio of the **P2/P3** products. As observed before for the optimisation of the conditions with **L18** (*vide supra*) monomer **P3** is slightly under-represented, relative to **P2**, in nearly all cases. **L12** is an outlier regarding the correlation between the G/S ratio in its structure and the **P2/P3** ratio in the products, which is probably the result of the proportion of H units found in this lignin (33%).

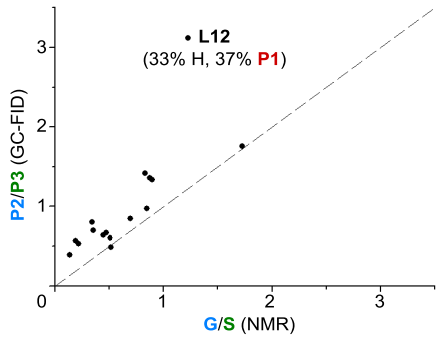



Fig. 4 Correlation between the G to S ratio determined by 2D HSQC and molar yield ratio between **P2** and **P3** as determined by GC-FID analysis of the low molecular weight fraction.

Overall, good product yields were observed from organosolv lignins **L1-L18** using this depolymerisation methodology (Fig. 3). Between most of the organosolv lignins **L1-L18** relatively small differences in yield were observed, with only methanosolv walnut lignin **L4** providing an exceptional 35.5 ±6.7 wt% combined yield of **P1-P3**. This lignin was prepared through low temperature extraction and contains the highest amount of β-O-4 linkages. Moreover, nearly 90% of these β-aryl ether linkages are etherified (Table S3), showing that this does not hamper **P1-P3** yields. Somewhat lower yields (6.7 to 17.6 wt%) of **P1-P3** were obtained from pine and Douglas fir wood (**L5**, **L6**, **L8**, **L11**, **L13** and **L14**) while the product yields from the remaining organosolv lignins (excluding **L4**) ranged from 11.3 to 22.3 wt%. Interestingly, pine and Douglas fir lignins provided almost exclusively **P2**, which correlates perfectly with the nearly exclusive G content in the parent lignins. All the yields of **L1-L18** were significantly higher compared to any of the technical lignins **L19-L27,** which provided yields only up to 5.6 wt%.

**P1-3 yield correlation to structural characteristic of the parent lignins.** When the organosolv lignins are compared to the technical lignins the main striking difference lies within the structure. While the technical lignins have low overall β-aryl ether content, as determined by semi-quantitative analysis of the 2D-HSQC NMR spectra (up to 13 per 100 aromatic $C_9$ unit, Table S3), the organosolv lignins show a more native-like structure with higher β-aryl ether content. A general trend can be observed between the **P1-P3** acetal yield and the total amount of β-aryl ethers (Fig. 5a, using the sum of β-O-4OH and β-O-4OR as both were previously shown to be hydrolysed by acid[7]). A good correlation is seen in the 0-25 β-aryl ether content per 100 aromatic $C_9$-units range as well as for lignins (**L1**, **L2** **L3** and **L4**) obtained from the same source with methanol as extraction solvent (walnut, Fig. 5b). This correlations provides that the expected total yield of **P1-P3** corresponds roughly to 0.4-0.5 times the β-aryl ether content (per 100 $C_9$ units) of the parent lignin.

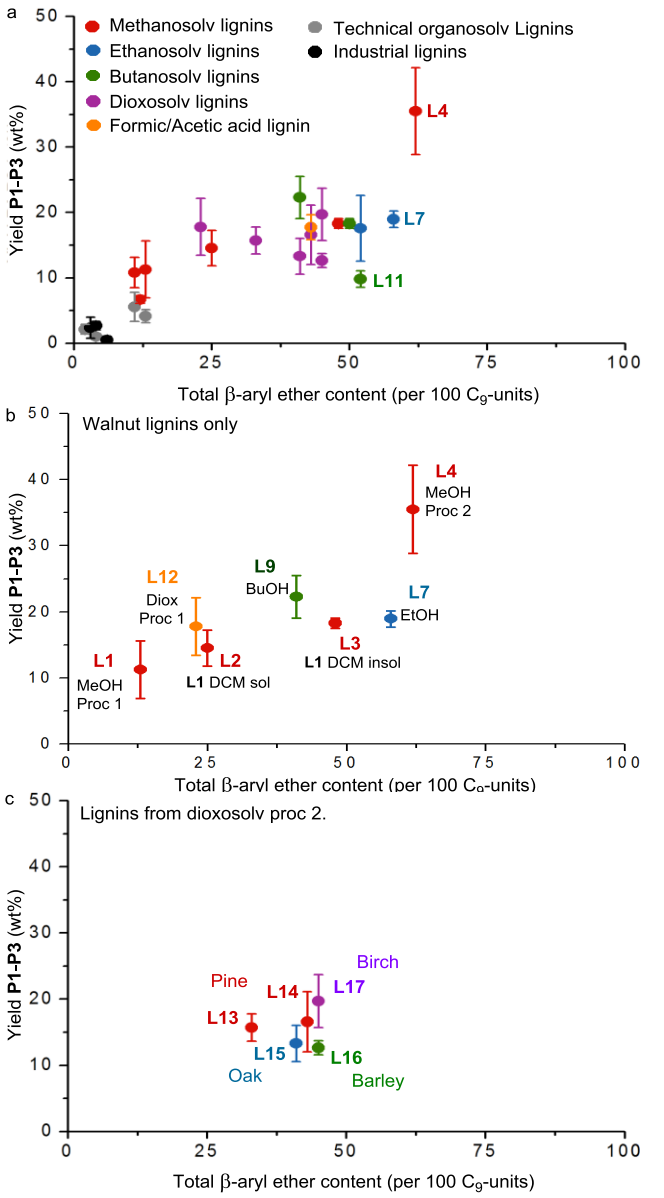



Fig. 5 a) Comparison between yields of product **P1-3** and the amount of total β-aryl ether linkages relative to aromatic signals in the lignin starting material. b) Showing only lignins originating from extractions from walnut shells. c) Showing only lignins obtained by dioxosolv procedure 2 from different biomass sources.

The total yield of **P1**-**P3** from lignin extracted using the same extraction methodology yielded a less clear trend due to these lignins having a reasonably similar β-aryl ether content (Fig. 5c). Further lignins in the 25-60 β-aryl ether content per 100 aromatic $C_9$-units range (Fig. 5a) do not share the same, for the other lignins seemingly linear correlation between the β-aryl ether content and the yields for **P1**-**P3**. The comparison between the yields of **P1**-**P3** with other lignin characteristics such as molecular weight and other linkages did not show any clear trends (Fig. S73-79). These results indicate that other unidentified factors apart from solely the β-aryl ether content play a role. This could be related to the different plant sources and factors specific to the extraction methods. For example, one outlier (**L11**) gave significantly lower yields than expected given its β-aryl ether content. This lignin was obtained through an *n*-butanol pretreatment process and the lower yield of monomers in this case when comparing to, for example, softwood dioxasolv lignins **L13-14**, can, at least in part, be explained by significant incorporation of butyl ethers into the starting lignin structure which is not corrected for by the wt% calculations. Also, the occurrence of other linkages (e.g. 5-5, β-5. β-β, etc) which are not cleaved by the methodology used here[5b], were not taken into account in this research. Due to selectivity for the applied methodology for the cleavage of β-aryl ether linkages, **P1**-**P3** are only released when a $C_9$-unit in the lignin structure is flanked by two such linkages (or is present as a phenolic end group).[4f] This leads to fragments containing other linkages becoming short oligomers with end-groups that are formed from the cleavage of a β-aryl ether linkage. With the current methodology, these end groups would be a phenol and a C2-acetal that correlates to products **P1**-**P3**. To test this hypothesis, the residue after extraction was analysed by 2D-NMR clearly revealing such end-groups (Fig. 1c and 1d). Similarly, Hibbert-ketone end-groups were recently observed following acidolysis.[5h] The deviations from the general "yield compared to β-O-4 content trend" observed in Fig. 5 may therefore also be explained by the relative positioning of β-O-4 linkages with regard to each other in the overall structure. For example, if the lignin contains regains with a high concentrations of β-O-4 linkages this will results in higher overall monomer yield compared to lignins in which the β-O-4 linkages are regularly distributed. Overall, the total β-aryl ether content seemed the main factor affecting the monomer yield. Such observation were previously hinted at in studies utilizing mild lignin depolymerisation methodologies but typically with smaller sample sizes.[4h,5b,15]

**Other low-molecular weight products.** Apart from products **P1**-**3** the GCMS traces (representative GCMS in Fig. S80) showed additional minor low molecular weight products of which several could be identified based on earlier studies (Fig. 6, Table S4, **P4**-**9**). These are ethylene glycol ketal products resulting from the reaction of released Hibbert-ketones[7], corresponding to side-products from the β-aryl ether cleavage via different pathways, and ethylene glycol.[5b,16] These Hibbert-ketones are formed via a cleavage pathway that, unlike the formation of **P1**-**3**, does not involve the loss of formaldehyde and which was previously established to be a minor pathway when $Fe(OTf)_3$ was used for β-aryl ether cleavage.[5d]
These products product were quantified using calculated response factors (Table S4).[17] They were observed in relatively small amounts (up to 2.6 wt%) and typically in 1-20% compared to the yield of parent major compounds **P1**-**3** demonstrating that these are indeed likely side-products from β-aryl ether cleavage via a minor cleavage pathway.[5b,16]

**Dimeric side-products.** With the help of products obtained from model compounds studies performed and reported on previously, **P10** and **P11** were also identified (Fig 6.).[5b,5d] Stilbene **P10** originates from β-5 linkages in the original lignin which has undergone ring-opening and loss of formaldehyde, while the acetal and phenol flanking groups are likely the results of the cleavage of flanking β-aryl ether linkages. This product was especially observed in relatively high amounts (up to 2.5 wt%) in G-rich lignins, which contain a significant amount of β-5 units such as **L5**, **L6**, **L8**, **L12**, **L13**, **L14** and **L21**. Additionally, **P10** could be identified in trace quantities in product mixtures obtained from **L4**, **L16** and **L18**. The two main diastereomeric forms of **P11** results from the epimerization of a β-β linkage (for the original stereochemistry of the β-β motif see Fig. 1).[5b,5d] Due to its stability and GC retention time (well separated from other products) it is easily detected and could be found in all product mixtures obtained from S-containing lignins, even in those with relatively low β-β content. It was particularly abundant in mixtures obtained from **L1**, **L2**, **L3**, **L7**, **L9**, **L10**, **L17** and **L18** (up to 5.7 wt%, which were all relatively high in S and β-β linkages. These findings demonstrate a good correlation between the dimeric products identified and the original lignin structure as determined by 2D-HSQC NMR spectroscopy.

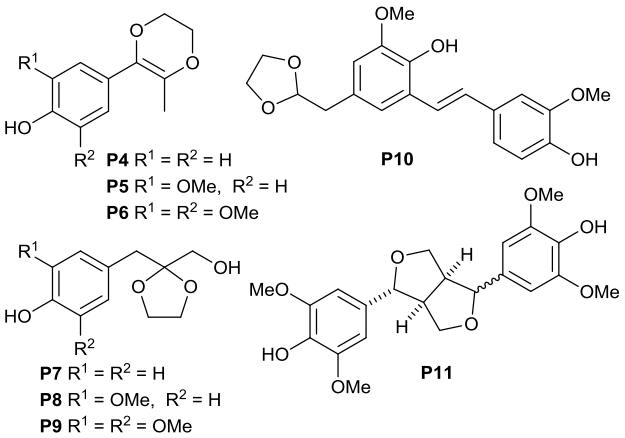



Fig. 6 Additionally, identified low molecular weight minor products from lignin depolymerisation reactions. **P4**-**P9** arising from cleavage of the β-O-4 through a different pathway and **P10** and **P11** from modification of β-5 and β-β linkages respectively.[5b,16]

## Conclusions

This study demonstrates the applicability and limitations of a mild lignin depolymerization method that uses acidolysis in combination with stabilization of reactive intermediates with ethylene glycol to produce phenolic acetal products **P1**-**P3**. Organosolv lignins that have been extracted using mild procedures provided the highest yields and are most suitable for the production of **P1**-**P3**. This correlates directly to the observed high β-aryl ether content in such lignins. The β-aryl ether content drops significantly as harsher extraction conditions are employed. This observation confirms that very likely only β-aryl ethers are cleaved under these depolymerisation conditions. A maximum yield of 35.5 ±6.7 wt% **P1**-**P3** was obtained from a lignin obtained via a mild methanosolv extraction of walnut shells (**L4**). This is one of the highest yields yet obtained for such a small selection of products, especially from isolated lignins. Noteworthy, is also the fact that 16.5 wt% of only **P2** could be obtained when pinewood dioxasolv lignin was used (**L13**). However, these lignins were only obtained in relatively low yields from their respective lignocellulose sources. Butanosolv lignins on the other hand can be obtained in much higher yields and still provide high yields of **P1**-**P3**. As observed previously,[8] a high content of etherified β-O-4 linkages did not hamper the yields of **P1**-**P3**, compared to other organosolv lignins. In addition to the very close correlation between the ratio **P1** : **P2** : **P3** to the H : G : S ratios found in the lignin substrates, the observed minor depolymerisation products also correlated well to the corresponding lignin structures.

Overall, this study shows that a direct relationship exists between the structure of the lignin used and the product yields obtained. This highlights the importance of carefully selecting the lignocellulose source as well as adjusting lignin extraction procedures in order to obtain starting materials ideal for efficient depolymerization.

## Experimental

**Commercial and externally obtained lignins.** Alkali kraft lignin (**L25**) and lignin sulfonate sodium salt (**L27**) were obtained from Aldrich. Technical ethanosolv lignins[9] from beech (**L19**), poplar (**L20**), spruce (**L21**) and Alcell (**L22**)[18] lignin were obtained from ECN (Petten, The Netherlands). Indulin-AT(**L23**) was from Meadwestvaco specialty chemicals, US. Kraft (**L24**) was provided in kind. Soda lignin Protobind 1000 (**L26**, mixed wheat straw/Sarkanda grass) was obtained from GreenValue S.A., Switzerland.

**Previously reported lignin extraction procedures.** The procedures for the isolation of walnut methanosolv (methanosolv procedure 1, **L1**-**3**)[5b], pine methanosolv (methanosolv procedure 1, batch 1 and 2, **L5**-**6**)[5b], ethanosolv (walnut and douglas fir, **L7**-**8**)[7], butansolv (walnut, beech and douglas fir, **L9**-**11**)[7] and walnut dioxasolv lignin (dioxasolv procedure 1, **L12**)[5a], were previously described. For extraction yields, see Table 1.

**Dioxasolv lignins by procedure 2 (birch, oak, barley straw, pine, L13-17).** The biomass is suspend in a solution of dioxane/water (9 : 1) containing 0.2 M HCl at a consistency of 8-10 mL per g of biomass. The mixture is then gently refluxed for 1 hour under $N_2$ atmosphere, cooled and filtered. The solid pulp is washed with a small portion of dioxane/water (9 : 1) or acetone/water (9 : 1). The filtrate is then concentrated in vacuo to give a gummy residue which is dissolved in acetone/water (9 : 1, 1 volume) and added to rapidly stirring water (10 volumes) to precipitate the lignin which is recovered by filtration. The crude lignin is then either allowed to air dry or is dried over $CaCl_2$ under vacuum overnight. The crude lignin is then dissolved in acetone/methanol (9 : 1, 1 volume) and added slowly to rapidly stirring $Et_2O$ (10 volumes) to precipitate the lignin which is collected by filtration and air dried. For extraction yields, see Table 1.

**Methanosolv lignin procedure 2 (walnut, L4).** Ground walnut shell (30 g, 16/30 mesh) is placed in a an Ace pressure tube (about 185 mL) and methanol/water (95 : 5, 120 mL) containing 0.2 M HCl is added. The tube is then sealed and the bottom half is placed in an oil bath set at 90 °C creating a gentle reflux in the tube. The mixture is heated for 6 hours, cooled and filtered. The solid residue is washed with additional methanol/water (95 : 5, about 120 mL), concentrated in vacuo to approximately 20-30 mL and added to rapidly stirring water (300 mL). The precipitated lignin is collected by filtration and air dried. For extraction yields, see Table 1.

**CIVM lignin (oak, L18).** The biomass is heated at 104 °C in a mixture of formic acid/acetic acid/water (3 : 5 : 2) for 5 hours and then cooled, filtered and the solid washed with acetic acid/water (9 : 1). The filtrate is then concentrated in vacuo, taken up in acetic acid/water (1 volume) and added to rapidly stirring water (10 volumes). The crude lignin is collected by filtration, washed with water and air-dried. The crude lignin is then dissolved in 0.5 M NaOH (15 mL/g), stirred for 2 hours at room temperature and then acidified with 1 M HCl (pH < 1). The precipitated lignin is collected by filtration, washed with water and air-dried. The lignin is then dissolved in acetone/methanol (9 : 1, 1 volume) and added slowly to rapidly stirring $Et_2O$ (10 volumes) to precipitate the lignin which is collected by filtration and air dried (overall yield 7 wt%). For extraction yields, see Table 1.

**General depolymerisation procedure.** Lignin (50 mg, **L1**-**L27**) was weighed out in a 20 mL microwave vial, equipped with a magnetic stirring bar. Internal standard (n-octadecane, 20 µL, 5 µmol, from an 0.25 M stock solution in 1,4-dioxane), ethylene glycol (15 µL, 33 wt%) and 900 µL 1,4-dioxane was added. The vial was sealed using a septum cap and the obtained solution was stirred and heated 140 °C. Iron(III)triflate was added by syringe through the septum from a 90 mg/mL stock solution in 1,4-dioxane (100 µL, 4.5 wt%). The reactions were stirred for 15 minutes after which the reaction was rapidly cooled on ice. The solutions were filtered over a plug of celite and the filtrate was concentrated under

high vacuum at 30 °C in an Univapo 150 ECH rotational vacuum concentrator. The remaining sticky solid was suspended in dichloromethane (vortexed and sonicated) after which 10 volume equivalents of toluene was added and again extensively mixed by vortex and sonication. The solution was centrifuged for 10 minutes at 13400 rpm using an Eppendorf minispin tabletop centrifuge and the liquid was separated from the solid by pipette. This extraction was repeater three times. The combined liquid was filtered over a plug of celite and concentrated under high vacuum at 30 °C in an Univapo 150 ECH rotational vacuum concentrator. The remaining oil was used for GC-FID analysis by dilution in DCM for quantification of acetal products P1-3 (Scheme S1) as well as GC-MS for identification. For the reaction for the optimization of varying reaction times and temperature for the depolymerisation of lignin **L19**, GPC measurements were performed on the reaction residue after the extractions (10 mg/ml solution in THF, see Figures S26-S27). For the depolymerisation reactions with different lignins, GPC analysis was performed on the mixture obtained after the reactions as well as the extracted and residual fractions (10 mg/ml solution in THF, Figures S28-S53). This analysis was not performed for lignin L6 and was not possible for the solids from the depolymerisation reactions of **L25** and **L27** due to insolubility in THF.

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13 Fe(OTf)3 under these conditions is assumed to be hydrolysed to liberate TfOH. Nevertheless it gives higher yields as observed in a comparative study found in Ref 5d.

 

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